

Summary Report for the Initiation of Compact Development for Particles with 425-micron Kernels

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1.0 Introduction

The purpose of this research was the initiation of overcoating TRISO particles with 425 μm kernels. In the AGR-1 task, the overcoating process was optimized for particles with an outer diameter (OD) of 780 μm and a 350 μm kernel. Therefore it needed to be determined how well the overcoating process used to fabricate AGR-1 compacts would perform on particles with an 855 μm OD and a 425 μm kernel. The matrix properties and overcoating procedures were altered from the AGR-1 processes in order to attempt to optimize the overcoating of TRISO particles with 425 μm kernels. This report summarizes the changes that were made to the matrix and the overcoating process in order to achieve successful overcoating of the larger particles.

2.0 Experimental

Based on the knowledge and experience gained from making AGR-1 compacts, it was determined that three variables should be changed in order to achieve acceptable overcoating of 855 μm OD TRISO particles. The three variables were: (1) matrix age/residual solvent content, (2) percent synthetic graphite in the matrix, and (3) the use of methanol instead of ethyl alcohol as the solvent used in making the matrix. Combining the data gathered from changing these variables with previous overcoating experience should lead to the eventual fabrication of within-specification compacts (although fabrication of compacts was not part of this SOW). With each of these changes standard overcoating runs were performed and the amount of each size fraction of overcoated particles was recorded. Changing of these variables not only helped to determine how to most efficiently overcoat particles with 425 μm kernels, but also increased understanding of the overcoating process in general.

2.1 Matrix age and residual solvent content

First, matrix age was considered, or the days elapsed between the date of matrix formation and the date of overcoating. During AGR-1 it was learned that the addition of methanol to overcoated particles, via a physisorbed monolayer, aided in the compacting process. The adsorbed methanol increased the malleability of the overcoat, which allowed it to flow more easily into the void spaces between particles. This increased malleability, in turn, decreased the compacting pressure and also allowed compacting to be performed at room temperature. A decrease in compacting pressure creates less force on the TRISO particles, thereby preventing them from moving and coming in contact with other TRISO particles. This lack of TRISO particle touching led to essentially zero broken SiC layers in the final AGR-1 compacts. Clearly the presence of methanol in the overcoat had a positive impact on compacting, but would it also play a role in overcoating as well? Methanol is deposited into the overcoater during the overcoating process, but the matrix itself has some amount of residual solvent which may influence the level of overcoating taking place. The influence of residual solvent, which was ethyl alcohol, in the matrix on overcoat thickness generation was not investigated prior. This solvent will evaporate over time, so overcoating with fresh matrix versus one that is many days old could have an impact on overcoat thickness generation. This was tested

by overcoating with matrix batch GKrs 060606, which was made in June 2006, and a matrix made just prior to overcoating.

2.2 Synthetic graphite addition to the matrix

The second variable that was changed was the amount of synthetic graphite in the matrix. It was found that the matrix portion of the AGR-1 compacts had a lower than expected density of approximately 1.1 g/cc. It was thought that this density could be increased by increasing the percentage of synthetic graphite in the matrix, as the synthetic graphite is denser than the natural graphite component. The impact of the additional synthetic graphite on overcoating was not known, and was therefore tested here.

Matrix batch GKrs 073107 was made in the same manner as the matrix used for AGR-1, except that the amount of synthetic graphite used was increased by 4 g. The matrix formulation used for AGR-1 overcoating and compacting utilized a 64:16:20 ratio of natural graphite, synthetic graphite, and resin, respectively. An AGR-1 batch of matrix consisted of 128 g of natural graphite, 32 g of synthetic graphite, and 40 g of resin. Matrix batch GKrs 073107 used 36 g of synthetic graphite instead of 32 g.

2.3 Methanol replacement of ethyl alcohol as matrix solvent

The third variable changed was the solvent used in the making of the matrix. In the AGR-1 project ethyl alcohol was the solvent used in the making of the matrix. The role of the solvent is to dissolve the resin and allow it to form a thin layer on the particles of natural and synthetic graphite. Matrix is also referred to as a “resinated powder” for this reason. The thermosetting resin is soluble in both ethyl alcohol and methanol. However, the vapor pressures of these solvents are different, which will directly affect the amount of residual solvent in the matrix prior to overcoating. The unknown influence on overcoating of residual solvent in the matrix has already been discussed.

Matrix batch GKrs 092107 was made with the original 64:16:20 ratio, but methanol was used as the solvent instead of ethyl alcohol. In making the matrix the two graphite powders are combined into a plastic container with a screw-top lid. Next 1000 mL of solvent is added to the plastic container; the solvent has always been ethyl alcohol, but was switched to methanol for this batch. The resin is then added to the container, and the contents are then mixed on a jar mill. After mixing the contents are poured into a shallow pan and allowed to dry into a “cake”. Once dry the cake is ground into a powder. This powder can correctly be identified as matrix or resinated powder.

The drying period takes approximately 24-hours for either ethyl alcohol or methanol, but the residual amount of solvent in the matrix is affected by the vapor pressure of the solvent. The vapor pressure of ethyl alcohol at 25°C is 0.08 atm, while the vapor pressure of methanol at the same temperature is 0.17 atm. The vapor pressure of methanol is more than twice that of ethyl alcohol, meaning it has a higher rate of vaporization. This higher rate of vaporization indicates there will be less residual solvent in the matrix.

2.4 Glow discharge mass spectrometry (GDMS) of resin

The thermosetting resin used in making the matrix has a shelf life of six months, after which time the viscosity of the resin can change due to the formation of solids. A new Durite SC1008 resin was ordered from Borden Chemical. The impurities of the resin were measured by first forming a char of the resin in a vacuum furnace at 600°C. The char was then sent to Shiva Technologies for GDMS analysis for the elements called out in the AGR-1 compact specification. The results are shown here in Table 1.

Table 1. Impurity analysis of resin batch LK7BD0051

impurity	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni
ppm wt.	0.39	8.9	0.09	0.01	0.72	0.05	1.1	0.05	0.13

3.0 Results and Discussion

3.1 Selection of TRISO particles for overcoating

The first step in the overcoating process was selection of TRISO particles with the appropriate OD of 855 μm . Unfortunately no particles with this exact outer diameter were available. Therefore, DUN350-27T TRISO particles were selected for initial overcoating development. These TRISO coated 350 μm diameter kernels have a mean outer diameter of 821 μm , making them the most representative particles currently available given the expected outer diameter of 855 μm for the 425 μm kernel TRISO. The DUN350-27T particles were tested for size and shape and the results are shown in Figure 1.

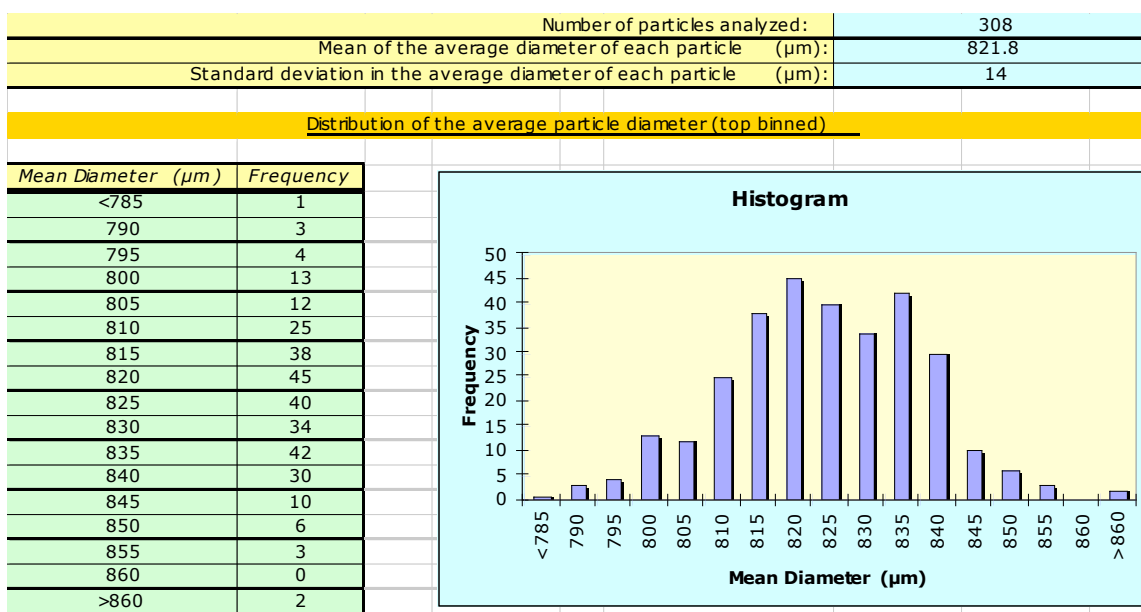


Figure 1. Size data for DUN-350-27T particles

3.2 Overcoating variable 1—aged matrix

DUN350-27T particles were overcoated with matrix batch GKRS 060606; a matrix batch that was used last year for experimental overcoating runs. Overcoating results were very poor in that essentially no overcoating took place. The matrix did not adhere to the OPyC layer of the particles even though higher than typical methanol volumes were used during overcoating. It was found that the age of the matrix, and in particular, the lack of inherent moisture in the matrix was probably responsible for these poor overcoating results.

The impact of matrix age was further explored by revisiting the AGR-1 overcoating runs and determining the days that had elapsed from the date of matrix production to the date of overcoating. It was thought that there may be a correlation between successful overcoating runs where large quantities of correctly sized overcoated particles were formed and fresh matrix that had high levels of residual solvent. Tables 2-5 show the days elapsed from matrix manufacture to overcoating and overcoated particle yields for the four batches of AGR-1 particles. In the tables MMD = matrix manufacturing date and DOO = date overcoating occurred.

Table 2. Baseline (46T) matrix age and overcoated particle yields

	MMD	DOO	Days elapsed	plus 18 yield (g)	
46T	121405	13106	47	28.63	
	121405	13106	47	18.45	
	121405	13106	47	13.23	
	121405	13106	47	9.30	
	121405	13106	47	14.20	
	121405	20106	48	29.53	
	121405	20106	48	18.62	
	121405	20106	48	28.98	
	121405	20106	48	27.34	
	121405	20106	48	23.53	
	121405	20606	53	11.66	
	121405	20606	53	24.44	
	121405	20606	53	26.80	
	121405	20606	53	23.43	
	121405	20606	53	23.72	
	121405	20606	53	27.36	
	121405	20606	53	19.00	
	121405	20606	53	17.90	
	121405	20906	56	14.92	
	121405	20906	56	16.20	
				20.86	average

MMD = matrix manufacturing date and DOO = date overcoating occurred

Tables 3. Variant 1 (47T) matrix age and overcoated particle yields

	MMD	DOO	Days elapsed	plus 18 yield (g)	
47T	30306	30806	4	13.72	
	30306	30806	4	27.84	
	30306	30806	4	29.43	
	30306	30806	4	29.56	
	30306	30806	4	30.13	
	30306	30906	5	29.00	
	30306	30906	5	28.30	
	30306	30906	5	27.75	
	30306	30906	5	27.81	
	30306	30906	5	30.33	
	30306	31306	9	29.53	
	30306	31306	9	29.86	
	30306	31306	9	29.34	
	30306	31306	9	28.43	
	30306	31406	10	27.14	
	30306	31406	10	26.00	
				27.76	average

MMD = matrix manufacturing date and DOO = date overcoating occurred

Table 4. Variant 2 (48T) matrix age and overcoated particle yields

	MMD	DOO	Days elapsed	plus 18 yield (g)	
48T	30906	41006	31	23.86	
	30906	41006	31	22.31	
	30906	41106	32	23.37	
	30906	41106	32	21.79	
	30906	41106	32	24.18	
	30906	41106	32	28.35	
	30906	41206	33	27.20	
	30906	41206	33	23.95	
	30906	41206	33	25.08	
	30906	41306	34	26.56	
	30906	41306	34	28.03	
	30906	41306	34	26.94	
	30906	41306	34	26.36	
	30906	41306	34	26.60	
	30906	41306	34	24.39	
				25.26	average

MMD = matrix manufacturing date and DOO = date overcoating occurred

Table 5. Variant 3 (49T) matrix age and overcoated particle yields

	MMD	DOO	Days elapsed	plus 18 yield (g)	
49T	30906	51506	66	28.00	
	30906	51606	67	25.07	
	30906	51606	67	27.13	
	30906	51606	67	23.72	
	30906	51606	67	26.02	
	30906	51606	67	24.72	
	30906	51606	67	26.50	
	51606	51706	1	19.75	
	51606	51706	1	28.37	
	51606	51706	1	26.40	
	51606	51706	1	29.79	
	51606	51706	1	22.60	
	51606	51806	2	25.72	
	51606	51806	2	27.64	
	51606	51806	2	27.90	
	51606	51906	3	28.11	
	51606	51906	3	27.13	
				26.15	average

MMD = matrix manufacturing date and DOO = date overcoating occurred

On average, the highest overcoated particle yield occurred with the variant 1 (47T) particles where an average overcoating run yielded 27.76 g of correctly sized overcoated particles. The days elapsed between MMD and DOO ranged from 4 to 10 days. The poorest overcoating results were found with the baseline (46T) particles where an overcoating run yielded 20.86 g of overcoated particles. Here, the days elapsed between MMD and DOO was 47 to 56 days. Based on the results for 46T and 47T it appears that matrix age has some impact on overcoating run yield. The influence of matrix age is further supported by the overcoating results of variant 3 (49T) particles. The overall average for all the overcoating yields was 26.15 g, but there is a large spread in days elapsed from MMD to DOO for these particles; 1-67 days. If the overcoating yields are averaged for the 1-3 day data the mass of overcoated particles per run was 26.34 g. The average yield for the overcoating runs made with 66-67 day old matrix was 25.88 g.

If an X-Y scatter curve is used to plot the days elapsed between MMD and DOO are plotted against mass of +18 overcoated particles yielded, it appears that a downward trend is observed, as shown in Figure 2. There is a large scatter in the data, so the correlation between matrix age and overcoating yield is not strong. However it is in agreement with what was observed in overcoating of the DUN-350-27T particles using matrix that was approximately 15 months old. In the data shown in Figure 2 the oldest matrix used was 67 days removed from its MMD. The matrix used to overcoat 27T was ~450 days old. It is conceivable that if additional data was available for the region between 67 to 450 days that the trend line in Figure 2 would indeed show a downward slope and the correlation between matrix age and poor overcoating results would

strengthen. It is believed that the poor overcoating results are due to a lack of solvent inherent to the matrix. Another possibility is that the resin in the matrix may have undergone a chemical change and be less tacky and able to adhere to the OPyC of the TRISO particles. More research is needed in the area of matrix age and resin chemistry; this is an area for future work.

3.3 Overcoating variable 2—additional synthetic graphite

Overcoating of DUN-350-27T particles was repeated using the fresher batch of matrix, GKrS 073107, that was prepared at the end of July. This batch of matrix contained 4 g extra of synthetic graphite. Overcoating was successful with the newer matrix. It is not yet determined what the target overcoat thickness is because no compacting has yet been performed on these particles. AGR-1 particles were overcoated to a thickness of approximately 160 microns (+18 sieve size), which yielded a packing fraction of 38%. Overcoating of the DUN-350-27T particles with GKrS 073107 led to the following masses of different overcoated particle masses, as shown in Table 6.

Table 6. Overcoating yields for DUN350-27T particles overcoated with GKrS 073107

Sieve size	Mesh opening (mm)	Mass (g)
+14	1.40	24.47
+16	1.18	20.53
+18	1.00	12.85

The size and shape of these overcoated particles were measured using an automated shadow scope. As stated, the correct overcoat layer thickness is not yet known, so both +16 and +18 size fractions were analyzed. Figure 3 shows the size data for the +16 size fraction and Figure 4 shows the size data. The +16 size fraction had a fairly non-Gaussian distribution for both size and shape, much less homogeneous than size and shape data previously recorded on AGR-1 overcoated particles. It was then determined that this non-Gaussian behavior was most likely the result of not tabling the particles prior to shadow scope analysis. Tabling helps to remove non-spherical particles and leftover chunks of matrix. Without tabling, these non-spherical particles and matrix chunks would be counted, thus skewing the size and shape data, as compared to the AGR-1 overcoated particles that were tabled.

The +16 and +18 size fractions were both tabled and size and shape analysis was performed on the now tabled overcoated particles. Figures 5 and 6 show the size and shape data (respectively) for the +16 particles, and Figures 7 and 8 show the size and shape data (respectively) for the +18 particles.

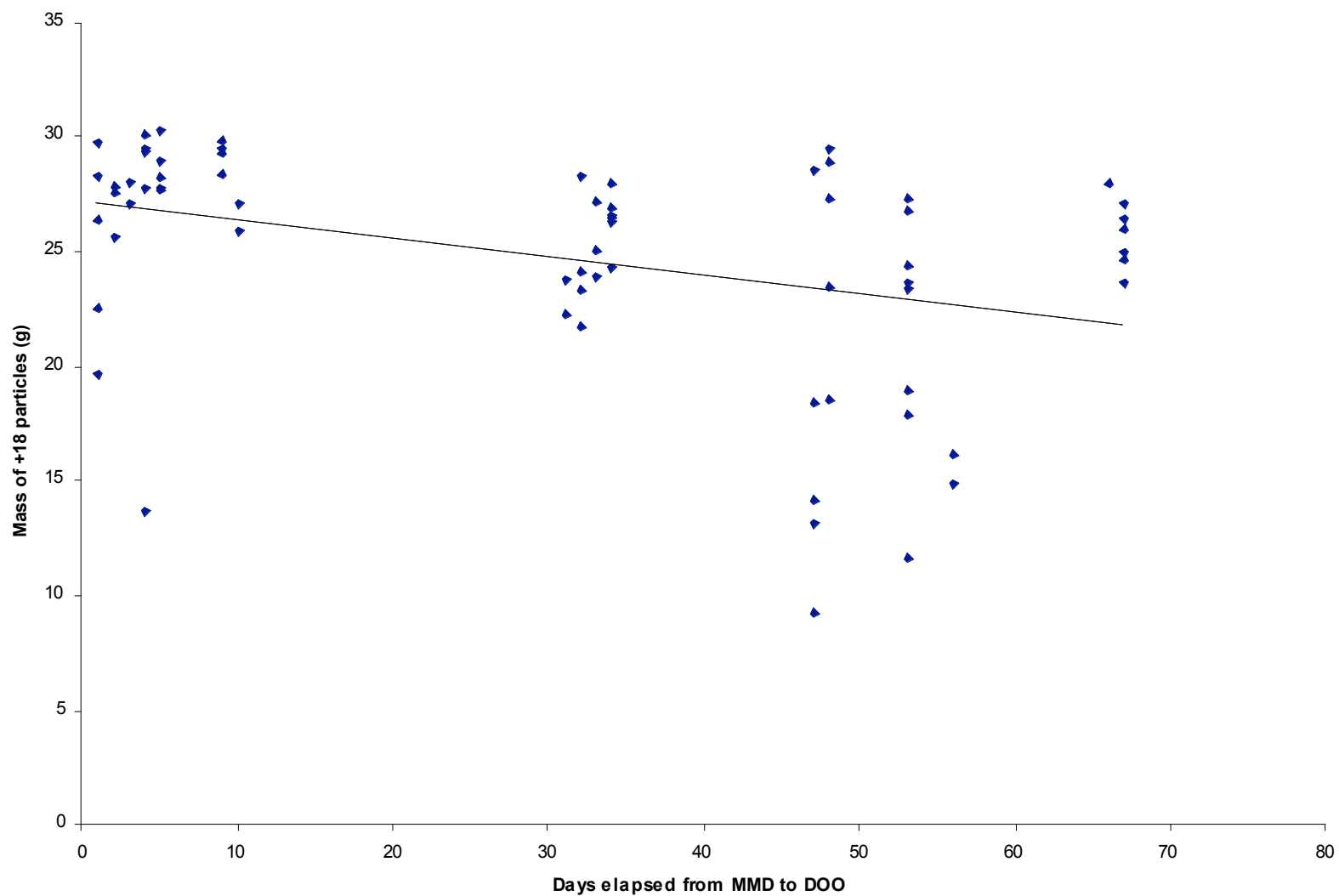


Figure 2. Relationship between matrix age and overcoated particle yield per overcoating run; +18 yields decrease with matrix age

Number of particles analyzed:	482
Mean of the average diameter of each particle (μm):	1262.0
Standard deviation in the average diameter of each particle (μm):	73

Distribution of the average particle diameter (top binned)

Mean Diameter (μm)	Frequency
<1100	1
1130	2
1160	15
1190	47
1220	85
1250	85
1280	79
1310	59
1340	40
1370	31
1400	22
1430	7
1460	2
1490	4
1520	2
1550	1
>1550	0

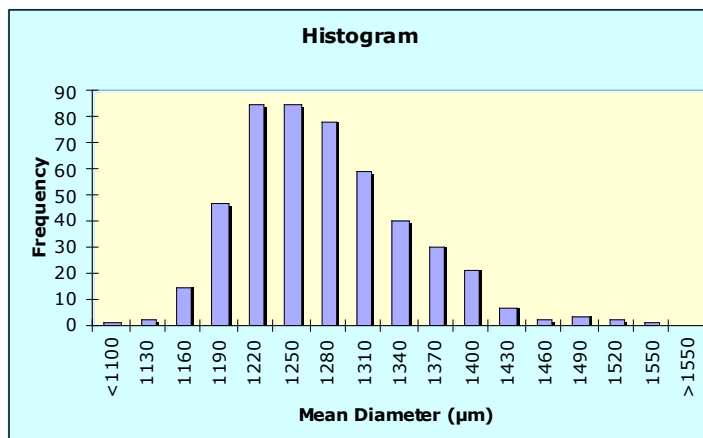


Figure 3. Size data for +16 size fraction, made with matrix batch GKrS 073107

Number of particles analyzed:	482
Average particle aspect ratio:	1.089

Distribution of the aspect ratio (top binned)

Aspect Ratio (D)	Frequency
1.005	0
1.015	0
1.025	5
1.035	18
1.045	33
1.055	56
1.065	62
1.075	70
1.085	50
1.095	41
1.105	38
1.115	28
1.125	18
1.135	11
1.145	7
1.155	8
1.165	3
1.175	4
1.185	4
1.195	2
1.205	2
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1.225	1
1.235	3
1.245	3
1.255	1
1.265	1
1.275	2
>1.275	9

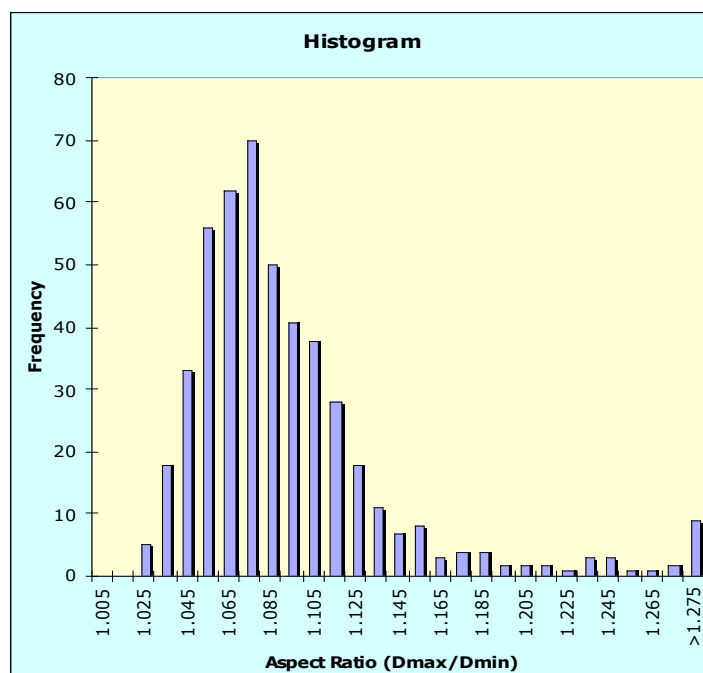


Figure 4. Shape data for +16 size fraction, made with matrix batch GKrS 073107

Number of particles analyzed:	469
Mean of the average diameter of each particle (μm):	1272.7
Standard deviation in the average diameter of each particle (μm):	69

Distribution of the average particle diameter (top binned)

Mean Diameter (μm)	Frequency
<1100	0
1130	0
1160	15
1190	30
1220	64
1250	82
1280	82
1310	75
1340	42
1370	36
1400	21
1430	12
1460	6
1490	1
1520	3
1550	0
>1550	0

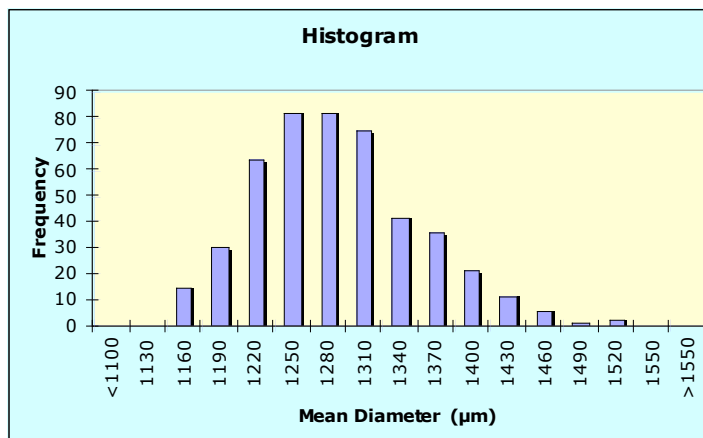


Figure 5. Size data for +16 size fraction after tabling, matrix batch GKRS073107

Number of particles analyzed:	469
Average particle aspect ratio:	1.083

Distribution of the aspect ratio (top binned)

Aspect Ratio (D)	Frequency
1.005	0
1.015	0
1.025	2
1.035	15
1.045	19
1.055	54
1.065	52
1.075	68
1.085	64
1.095	52
1.105	52
1.115	19
1.125	18
1.135	20
1.145	13
1.155	6
1.165	4
1.175	1
1.185	5
1.195	3
1.205	0
1.215	1
1.225	0
1.235	0
1.245	1
1.255	0
1.265	0
1.275	0
>1.275	0

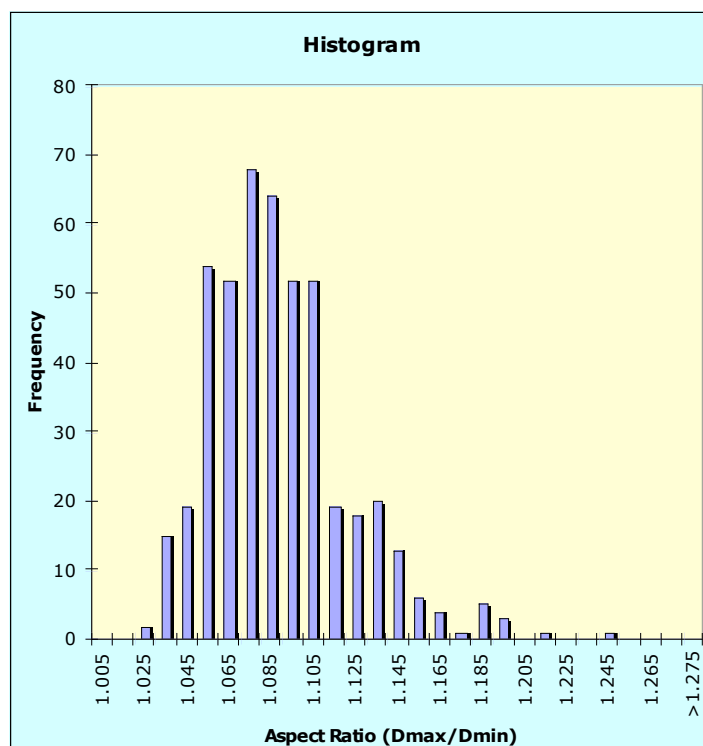


Figure 6. Shape data for +16 size fraction after tabling, matrix batch GKRS073107

Number of particles analyzed:	588
Mean of the average diameter of each particle (μm):	1150.4
Standard deviation in the average diameter of each particle (μm):	45

Distribution of the average particle diameter (top binned)

Mean Diameter (μm)	Frequency
<1000	0
1020	1
1040	5
1060	14
1080	21
1100	39
1120	63
1140	70
1160	114
1180	114
1200	80
1220	42
1240	15
1260	8
1280	0
1300	1
>1300	1

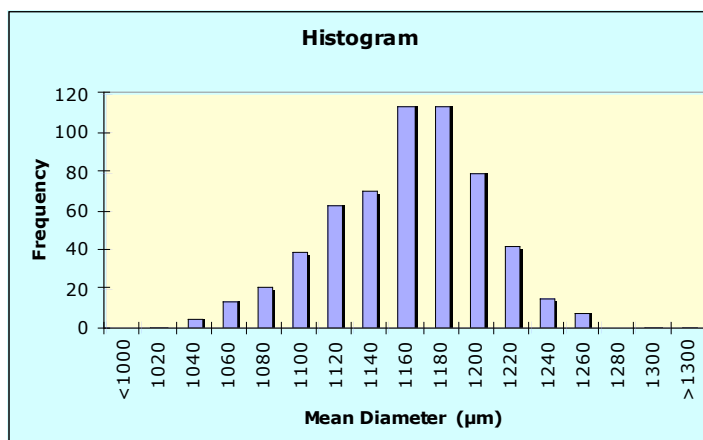


Figure 7. Size data for +18 size fraction after tabling, matrix batch GKrS073107

Number of particles analyzed:	588
Average particle aspect ratio:	1.085

Distribution of the aspect ratio (top binned)

Aspect Ratio (D)	Frequency
1.005	0
1.015	1
1.025	1
1.035	17
1.045	47
1.055	61
1.065	74
1.075	63
1.085	72
1.095	84
1.105	36
1.115	29
1.125	30
1.135	24
1.145	13
1.155	11
1.165	6
1.175	5
1.185	2
1.195	1
1.205	2
1.215	2
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1.255	0
1.265	0
1.275	1
>1.275	2

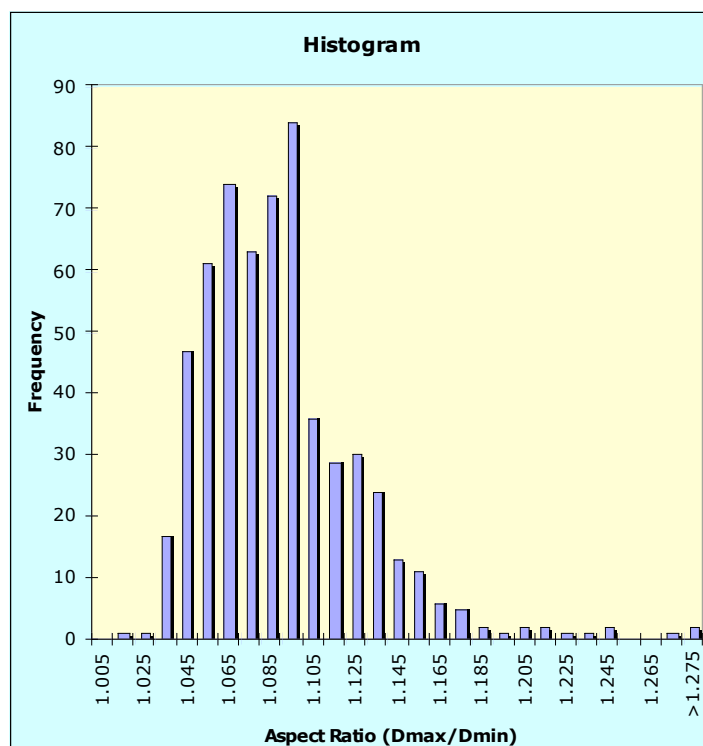


Figure 8. Shape data for +18 size fraction after tabling, matrix batch GKrS073107

Tabling the particles definitely helped to reduce the tailing seen in Figures 3 and 4. The sphericity of the particles also improved, going from 1.089 in the original particles to 1.083 after tabling. The mean average diameter of the particles is also important to note. The +16 particles, after tabling, had a mean average diameter of 1273 μm . The number 16 sieve has a screen opening of 1.18 mm (1180 μm) so the overcoated particle that comes to rest on a number 16 screen should be at least 1180 μm in diameter. The shadow scope measures the diameter of these +16 particles as 1273 μm , which is reasonable. The same trend is observed for the +18 particles. A number 18 sieve has a screen opening of 1.00 mm (1000 μm) so the diameter of a +18 particle should be greater than 1000 μm . The +18 particles measured here have a mean average diameter of 1150 μm .

The overcoat thickness of these particles is as follows. The base TRISO particles had a diameter of 821 μm , so the +16 particles, on average, had an overcoat thickness of 226 μm $[(1273-821)/2]$. The +18 particles had an overcoat thickness of 164 μm $[(1150-821)/2]$. The most desirable overcoat layer thickness for making within specification compacts is not yet known, but compacting of these overcoated particles will take place next fiscal year.

3.4 Overcoating variable 3—use of methanol as matrix solvent

Matrix batch GKRS 092107 was made using methanol as the thermosetting resin solvent instead of ethyl alcohol. The data outlined in Section 3.2 suggests that overcoating results can be influenced by the following: (1) the amount of residual solvent in the matrix or, (2) a chemical change in the resin itself that occurs over time. Overcoating of DUN-350-27T particles was carried out following the same overcoating procedures used while manufacturing AGR-1 compacts. The yields of the different sieve fractions of overcoated particles after two overcoating runs are shown in Table 7.

Table 7. Overcoating yields for DUN350-27T particles overcoated with GKRS 092107

Sieve size	Mesh opening (mm)	Mass (g)
+14	1.40	1.72
+16	1.18	25.03
+18	1.00	39.25

Here the fraction of +14 sized overcoated particles was reduced, as compared to the overcoating results shown in Table 6. The +14 size fraction was reduced by supplying less methanol to the overcoater during and overcoating run. The amounts of both the +16 and +18 size fractions were also increased. The results shown in Table 7 are comparable to overcoated particle yields found during AGR-1 particle overcoating and compacting. The use of methanol as the matrix solvent did not appear to negatively impact the overcoating process. However, three days had elapsed since MMD. As shown in Tables 2-5, sometimes the elapsed days between MMD and DOO in AGR-1 approached 67. The overcoating results using a methanol based matrix may be negatively impacted after this number of elapsed days (67). The effectiveness of an aged methanol based matrix in overcoating will be tested in the next fiscal year. It appears that the age of the matrix has an impact on the yield of +16 and +18 sized overcoated particles, but it is unclear at this

time whether this is due to a lack of residual solvent in the matrix, or a chemical change in the resin portion of the matrix.

4.0 Summary and Conclusions

The overcoating procedures developed for the AGR-1 compacts were based on a TRISO particle with a 350 μm kernel and an OD of 780 μm . The research presented in this report was focused on overcoating a larger OD TRISO particle while changing certain matrix properties and overcoating procedures. Unfortunately the kernel was still 350 μm , but the OD was 821 μm , about 30 μm smaller than the target TRISO particle with a 425 μm kernel.

Three variables were changed in order to determine their effect on overcoating of 821 μm OD TRISO particles, as well as help understand the overcoating process in general. The three variables were: (1) matrix age, (2) percent synthetic graphite in the matrix, and (3) matrix solvent. It was found that matrix age had a significant impact on overcoating yields, to the point of experiencing very little overcoat layer thickness development. A roughly 450 day old matrix was used in the overcoating process and found to provide little matrix addition to the TRISO particles. The overcoating results for the AGR-1 particles were reviewed and a weak correlation to matrix age and poor overcoating yields was found. However the oldest matrix used during AGR-1 was 67 days old, while the matrix used here was ~450 days old. More data points are needed between 67 and 450 in order to fully understand the relationship between matrix age and overcoating yields. It is believed that either the amount of residual solvent in the matrix or a chemical change in the resin portion of the matrix must be responsible for the poor overcoating results, if they are indeed correlated.

The amount of synthetic graphite appeared to have no effect on overcoating yields. A higher percentage of synthetic graphite in the matrix should provide a denser matrix in the compact, as the synthetic graphite is higher density than the natural graphite or resin components. Compacting of overcoated particles made from matrix with higher amounts of synthetic graphite will be performed next fiscal year.

The solvent used in making the matrix also does not appear to have an effect on the overcoating process. Methanol was used instead of ethyl alcohol in making matrix batch GKRS 092107. It was thought that methanol would vaporize more quickly out of the matrix, as the vapor pressure of methanol is more than twice that of ethyl alcohol. Methanol does indeed vaporize more quickly, but a negative impact on overcoating was not observed. This may be because the days elapsed between MMD and DOO were not sufficient.

The two main outcomes of this research were: (1) overcoating of particles with a 821 μm OD (which were meant to simulate a TRISO particle with a 425 μm kernel) is possible and yields similar to those found during AGR-1 were seen, and (2) the reason why matrix age affects overcoating needs to be researched further.